

Additive mixture for motor fuels and lubricants

The present invention relates to additive mixtures which
5 comprise, as component A, at least one additive having detergent
action and, as component B, at least one partially or completely
neutralized fatty acid. The invention further relates to the use
of these additive mixtures for additizing fuel and lubricant
compositions, and also to motor fuel and lubricant compositions
10 and concentrates which comprise this additive mixture.

The efforts to reduce damaging emissions in the combustion of
motor fuels, in particular of diesel fuels, have concentrated in
recent times on the reduction of sulfur dioxide emissions and
15 also the reduction of particle emissions, in particular in diesel
exhaust fumes. To reduce sulfur dioxide emissions, the sulfur
content in gasoline and diesel fuels has been reduced in recent
years in refineries by hydrotreatment, in which the fuel is
treated with hydrogen to reduce sulfur-containing components to
20 hydrogen sulfide. An undesired secondary effect of this
desulfurization is the destruction of polyaromatic and polar
components in the fuel. Expecially in the case of diesel fuels,
this has adverse effects, since diesel engines are
fuel-lubricated and, as a consequence of the reduction of the
25 natural lubricity of the fuel, the wear increased, in particular
in the region of the high pressure injection pumps. The wear
problem becomes even more significant when the fuels are used in
a mixture with gas to liquid (GTL) fuels or with renewable fuels
such as bioethanol, since these components have no
30 lubricity-improving properties at all.

To avoid wear, synthetic lubricity improvers, such as fatty acid
mixtures, their esters, amides or salts, are generally added to
the fuel.
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Motor fuels are also additized with detergents which are intended
to reduce carbon deposits caused by the fuel in the region of the
injection nozzles and orifices which, inter alia, in
direct-injection high-performance systems such as common rail,
40 pump-nozzle or pump-line-nozzle, impair the optimum formation of
a fine fuel mist and thus lead to increased fuel consumption and
emissions.

Additives having detergent action for improving the lubricity of
45 fuels are described, for example, in WO-A-96/23855. The additive
compositions described there comprise an N-acylated compound

which burns ashlessly and a carboxylic acid or a carboxylic ester and are intended to improve the lubricity.

WO-A-01/38463 describes the use of fatty acid salts of
5 alkoxyated oligoamines as lubricity improvers for mineral oil products.

A disadvantage of the additives and additive mixtures described in the prior art is that relatively high dosages are required to
10 achieve a lubricity-improving effect.

It is an object of the present invention to provide additive mixtures which successfully improve the lubricity of fuel and lubricant compositions even at relatively low dosages.

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We have found that this object is achieved in that, surprisingly, combinations of additives having detergent action and of partially or completely neutralized fatty acids exhibit a synergistic effect with regard to the improvement of lubricity
20 and, at the same time, the detergency of fuel and lubricant compositions.

The present invention therefore provides an additive mixture comprising

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i) as component A, at least one additive having a detergent action which has at least one hydrophobic hydrocarbon radical having a number average molecular weight (M_n) of from 85 to 20000 and at least one polar terminal group, and

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ii) as component B, at least one partially or completely neutralized fatty acid.

Preference is given to selecting the polar terminal group of
35 component A from

(a) mono- or polyamino groups having up to 6 nitrogen atoms where at least one nitrogen atom has basic properties,

40 (b) nitro groups, optionally in combination with hydroxyl groups,

(c) hydroxyl groups in combination with mono- or polyamino groups where at least one nitrogen atom has basic properties,

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(d) polyoxy-C₂-C₄-alkylene groups which are terminated by hydroxyl groups, mono- or polyamino groups where at least one nitrogen atom has basic properties, or by carbamate groups,

5 (e) carboxylic ester groups,

(f) groups formed by Mannich reaction of substituted phenols with aldehydes and mono- or polyamines and

10 (g) groups which are derived from carboxylic anhydrides and have hydroxyl and/or amino and/or amido and/or imido groups.

Additives containing mono- or polyamino groups (a) are preferably polyalkenemono- or polyalkenepolyamines based on polypropene or
15 on reactive (i.e. having predominantly terminal double bonds, usually in the β - and γ -positions) or conventional (i.e. having predominantly internal double bonds) polybutene or polyisobutene having an M_N of from 300 to 5000. Such additives based on reactive polyisobutene, which can be prepared from the polyisobutene
20 (which may contain up to 20% by weight of n-butene units) by hydroformylation and reductive amination with ammonia, monoamines or polyamines, such as dimethylaminopropylamine ethylenediamine, diethylenetriamine, triethylenetetramine or tetraethylenepentamine, are disclosed in particular in EP-A
25 244 616. When polybutene or polyisobutene having predominantly internal double bonds (usually in the β and γ positions) are used as starting materials in the preparation of the additives, the possible preparative route is by chlorination and subsequent amination or by oxidation of the double bond with air or ozone to
30 give the carbonyl or carboxyl compound and subsequent amination under reductive (hydrogenating) conditions. The amines used here for the amination may be the same as those used above for the reductive amination of the hydroformylated reactive polyisobutene. Corresponding additives based on polypropene are
35 described in particular in WO-A 94/24231, which is fully incorporated herein by way of reference.

Further preferred additives containing monoamino groups (a) are the hydrogenation products of the reaction products of
40 polyisobutenes having an average degree of polymerization P of from 5 to 100 with oxides of nitrogen or mixtures of oxides of nitrogen and oxygen, as described in particular in WO-A 97/03946, which is fully incorporated herein by way of reference.

45 Further preferred additives containing monoamino groups (a) are the compounds obtainable from polyisobutene epoxides by reaction with amines and subsequent dehydration and reduction of the amino

alcohols, as described in particular in DE-A 196 20 262 which is fully incorporated herein by way of reference.

Additives containing nitro groups, optionally in combination with
5 hydroxyl groups, (b) are preferably reaction products of polyisobutenes having an average degree of polymerization P of from 5 to 100 or from 10 to 100 with nitrogen oxides or mixtures of nitrogen oxides and oxygen, as described in particular in WO-A 96/03367 and WO-A 96/03479, which are fully incorporated herein
10 by way of reference. These reaction products are generally mixtures of pure nitropolyisobutanes (e.g. α,β -dinitropolyisobutane) and mixed hydroxynitropolyisobutanes (e.g. α -nitro- β -hydroxypolyisobutane).

15 Additives containing hydroxyl groups, optionally in combination with mono- or polyamino groups, (c) are in particular reaction products of polyisobutene epoxides, obtainable from polyisobutene having preferably predominantly terminal double bonds and an M_N of from 300 to 5000, with ammonia or mono- or polyamines, as
20 described in particular in EP-A 476 485, which is fully incorporated herein by way of reference.

Additives containing polyoxy-C₂- to C₄-alkylene groups (d) are preferably polyethers or polyetheramines which are obtainable by
25 reaction of C₂- to C₆₀-alkanols, C₆- to C₃₀-alkanediols, mono- or di-C₂-C₃₀-alkylamines, C₁-C₃₀-alkylcyclohexanols or C₁-C₃₀-alkylphenols with from 1 to 30 mol of ethylene oxide and/or propylene oxide and/or butylene oxide per hydroxyl group or amino group and, in the case of the polyetheramines, by subsequent
30 reductive amination with ammonia, monoamines or polyamines. Such products are described in particular in EP-A 310 875, EP-A 356 725, EP-A 700 985 and US-A 4 877 416, which are fully incorporated herein by way of reference. In the case of polyethers, such products also have carrier oil properties.
35 Typical examples of these are tridecanol butoxylates, isotridecanol butoxylates, isononylphenol butoxylates and polyisobutenol butoxylates and propoxylates and the corresponding reaction products with ammonia.

40 Additives containing carboxylic ester groups (e) are preferably esters of mono-, di- or tricarboxylic acids with long-chain alkanols or polyols, in particular those having a minimum viscosity of 2 mm² at 100°C, as described in particular in DE-A 38 38 918, which is fully incorporated herein by way of
45 reference. The mono-, di- or tricarboxylic acids used may be aliphatic or aromatic acids, and particularly suitable ester alcohols or ester polyols are long-chain representatives having,

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for example, 6 to 24 carbon atoms. Typical representatives of the esters are adipates, phthalates, isophthalates, terephthalates and trimellitates of isooctanol, of isononanol, of isodecanol and of isotridecanol. Such products also have carrier oil properties.

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Additives containing groups produced by conventional Mannich reaction of phenolic hydroxyl groups with aldehydes and mono- or polyamines (f) are preferably reaction products of polyisobutene-substituted phenols with formaldehyde and primary
10 mono- or polyamines, such as ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine or dimethylaminopropylamine. Such polyisobutene Mannich bases are described in particular in EP-A 831 141, which is fully incorporated herein by way of reference.

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Additives containing groups which are derived from carboxylic anhydrides and have hydroxyl and/or amino and/or amido and/or imido groups (g) are preferably corresponding derivatives of dicarboxylic anhydrides, more preferably of succinic anhydride.

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The polar group of component A is more preferably a group which is derived from carboxylic anhydrides and has hydroxyl and/or amino and/or amido and/or imido groups (g), in particular having amido and/or imido groups, i.e. N-acyl groups.

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Component A is preferably an acylated nitrogen compound (N-acyl compound) which burns ashlessly and has a polar group (g).

However, component A may, in addition to the preferred acylated
30 nitrogen compound (N-acyl compound) which burns ashlessly and has a polar group (g), also comprise one or more further compounds which correspond to the combination of hydrophobic hydrocarbon radicals with the abovementioned polar groups (a) to (f).

35 The hydrophobic hydrocarbon radical of component A is preferably a homo- or copolymer radical whose repeating units are derived from monomers which are selected from propene, n-butene and isobutene and mixtures thereof.

40 The homo- or copolymer radical is more preferably a polyisobutene radical. In particular, the homo- or copolymer radical is a "reactive" polyisobutene radical which differs from "low-reactivity" polyisobutenes by the terminal double bond content. Reactive polyisobutenes differ from low-reactivity
45 polyisobutenes in that they have not less than 50 mol%, preferably not less than 60 mol% and more preferably not less than 80 mol%, of terminal double bonds, based on the total number

- of polyisobutene macromolecules. The terminal double bonds may either be vinyl double bonds $[-CH=C(CH_3)_2]$ or else vinylidene double bonds $[-CH_2-C(=CH_2)-CH_3]$. Preference is given in particular to polyisobutenes which have uniform polymer backbones. Those
- 5 polyisobutenes in particular which are composed of at least 85% by weight, preferably at least 90% by weight and more preferably at least 95% by weight, of isobutene units have a uniform polymer backbone. Such reactive polyisobutenes preferably have a number average molecular weight in the range from 200 to 20 000.
- 10 Reactive polyisobutenes in particular which have a number average molecular weight in the range from 300 to 3 000, more preferably from 400 to 2 500 and most preferably from 500 to 1 500, for example a number average molecular weight of about 550, about 800, about 1 000 or about 2 300 are suitable for preparing fuel
- 15 additives. Reactive polyisobutenes in particular which have a number average molecular weight in the range from 1000 to 15 000, more preferably from 1300 to 12500 and most preferably from 2000 to 10 000, for example a number average molecular weight of about 1500, about 2000 or about 2300 are suitable for preparing
- 20 lubricant additives. Furthermore, the reactive polyisobutenes preferably have a polydispersity of less than 3.0, in particular less than 1.9 and more preferably less than 1.7 or less than 1.5. Polydispersity is the quotient of the weight average molecular weight M_w divided by the number average molecular weight M_N .
- 25 Examples of particularly suitable reactive polyisobutenes include the Glissopal brands from BASF AG, in particular Glissopal 1000 ($M_N = 1\ 000$) and Glissopal V 33 ($M_N = 550$) and Glissopal 2300 ($M_N = 2\ 300$) and their mixtures. Other number average molecular
- 30 weights may be attained in the manner known in principle by mixing polyisobutenes of different number average molecular weights or by extractive enrichment of polyisobutenes of certain molecular weight ranges.
- 35 Component A is preferably an N-acyl compound which burns ashlessly and is derived from a polar group (g) which is substituted by a homo- or copolymer radical. Preferred polar groups (g) and preferred hydrophobic hydrocarbon radicals are those mentioned previously. The acyl compound which burns
- 40 ashlessly is more preferably an N-acyl compound which is derived from polyalkenylsuccinic anhydrides and especially from polyisobutenylsuccinic anhydrides. Of particular interest in this connection are N-acyl compounds which are obtainable by reacting the anhydride with aliphatic polyamines, such as ethylenediamine,
- 45 diethylenetriamine, triethylenetetramine or tetraethylenepentamine. Such N-acyl compounds are described in

particular in US-A 4 849 572, which is fully incorporated herein by way of reference.

The polyisobutenylsuccinic anhydride is obtainable, for example, 5 by reacting conventional or reactive polyisobutene having M_N from 300 to 5 000 with maleic anhydride by thermal routes or via the chlorinated polyisobutene.

The acylated nitrogen compound which burns ashlessly and has a 10 polar group (g) is obtainable, for example, by reacting a carboxylic acid substituted by a hydrophobic hydrocarbon radical or a carboxylic acid derivative substituted by a hydrophobic hydrocarbon radical with an amine which has at least one NH or NH_2 group. Preference is given to reacting a carboxylic anhydride.

15 As detailed hereinabove, the carboxylic acid or carboxylic acid derivative is more preferably a dicarboxylic acid or a dicarboxylic acid derivative, preferably a dicarboxylic anhydride, in particular a succinic acid or succinic acid 20 derivative, preferably a succinic anhydride. Preference is given to polyalkenylsuccinic acids or polyalkenylsuccinic acid derivatives, preferably polyalkenylsuccinic anhydrides, especially polyisobutenylsuccinic anhydride.

25 The reaction of dicarboxylic acids or their derivatives, especially dicarboxylic anhydrides, with amines may result in product mixtures which comprise dicarboxylic monoamides, dicarboxylic diamides, ammonium salts of dicarboxylic monoamides, dicarboxylic monoamide monoesters, amidines and also dicarboxylic 30 mono- and diimides. Useful components A are both the individual acylation products mentioned and their mixtures. However, preference is given to dicarboxylic imides, in particular dicarboxylic monoimides.

35 For the reaction with the carboxylic acid or carboxylic acid derivative, useful amines are both monoamines, i.e. amines having only one amino function in the molecule, and polyamines, i.e. those having at least two amino functions in the molecule.

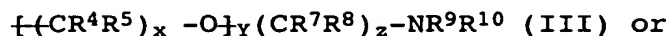
40 Useful monoamines are both primary and secondary aliphatic amines having from 3 to 10 carbon atoms, such as propylamine, butylamine, pentylamine, hexylamine, octylamine, diethylamine, dipropylamine, diisopropylamine, dibutylamine, cyclohexylamine, N-methylcyclohexylamine, N-ethylcyclohexylamine, piperidine, 45 piperazine and morpholine. Mixtures of monoamines are also suitable, in particular amine mixtures obtainable on the industrial scale, such as fatty amines, as described, for

example, in Ullmanns Encyclopedia of Industrial Chemistry, 6th edition, 2000 electronic release, chapter "Amines, aliphatic", which is fully incorporated herein by way of reference.

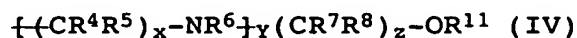
5 However, preference is given to using polyamines.

Examples of useful polyamines include those of the formula $NR^1R^2R^3$ where at least one of the R^1 , R^2 or R^3 radicals is a radical of the following formulae II, III or IV

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where

R^4 , R^5 , R^6 , R^7 , R^8 and R^{11} are each independently H or C_1 - C_6 -alkyl,

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R^9 and R^{10} are each independently H, C_1 - C_6 -alkyl or C_1 - C_6 -hydroxyalkyl,

x and z are each independently a number from 1 to 8 and

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y is a number from 0 to 8.

R^4 , R^5 , R^6 , R^7 , R^8 and R^{11} are preferably each H or methyl.

30 Those R^1 , R^2 and R^3 radicals which are not a radical of the formula II, III or IV are preferably H, C_1 - C_6 -alkyl, C_1 - C_6 -hydroxyalkyl or C_3 - C_8 -cycloalkyl, although at least one of the R^1 , R^2 and R^3 radicals has to be H.

35 In the above definition of the R^1 , R^2 , R^3 , R^4 , R^5 , R^6 , R^7 , R^8 and R^{11} radicals, C_1 - C_6 -alkyl is in particular methyl, ethyl, propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tert-butyl, pentyl or hexyl.

40 C_1 - C_6 -Hydroxyalkyl is in particular the aforementioned C_1 - C_6 -alkyl radicals substituted by a hydroxyl group.

C_3 - C_8 -Cycloalkyl is in particular cyclopropyl, cyclopentyl, methylcyclopentyl, cyclohexyl, methylcyclohexyl and cyclooctyl.

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More preferably, R^1 and R^2 are H and R^3 is a radical of the formula I where R^4 , R^5 , R^6 , R^7 , R^8 and R^{10} are each H.

Examples of useful polyamines include ethylenediamine,
 5 diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine, propylenediamine, dipropylenetriamine, tripropylenetetramine, tetrapropylenepentamine, pentapropylenehexamine, butylenediamine, dibutylenetriamine, tributylenetetramine, tetrabutylene-pentamine,
 10 pentabutylenehexamine, N,N-dimethylmethylenediamine, N,N-diethylmethylenediamine, N,N-dipropylmethylenediamine, N,N-dimethylethylene-1,2-diamine, N,N-diethylethylene-1,2-diamine, N,N-dipropylethylene-1,2-diamine,
 15 N,N-dimethylpropylene-1,3-diamine, N,N-diethylpropylene-1,3-diamine, N,N-dipropylpropylene-1,3-diamine, N,N-dimethylbutylene-1,4-diamine, N,N-diethylbutylene-1,4-diamine,
 20 N,N-dipropylbutylene-1,4-diamine, N,N-dimethylpentylene-1,5-diamine, N,N-diethylpentylene-1,5-diamine, N,N-dipropylpentylene-1,5-diamine, N,N-dimethylhexylene-1,6-diamine,
 25 N,N-diethylhexylene-1,6-diamine, N,N-dipropylhexylene-1,6-diamine, bis[2-(N,N-dimethylamino)ethyl]amine, bis[2-(N,N-diethylamino)ethyl]amine, bis[2-(N,N-dipropylamino)ethyl]amine,
 30 bis[3-(N,N-dimethylamino)propyl]amine, bis[3-(N,N-diethylamino)propyl]amine, bis[3-(N,N-dipropylamino)propyl]amine, bis[4-(N,N-dimethyl-amino)butyl]amine, bis[4-(N,N-diethylamino)butyl]amine,
 35 bis[4-(N,N-dipropylamino)butyl]amine, bis[5-(N,N-dimethylamino)pentyl]amine, bis[5-(N,N-diethylamino)pentyl]amine, bis[5-(N,N-dipropylamino)pentyl]amine, bis[6-(N,N-dimethylamino)hexyl]amine,
 40 bis[6-(N,N-diethylamino)hexyl]amine, bis[6-(N,N-dipropylamino)hexyl]amine and the like. Such polyamines are described in Kirk-Othmers "Encyclopedia of Chemical Technology", 2nd edition, Volume 7, pages 22 to 37, Interscience Publishers, New York (1965), chapter "Ethyleneamines".

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Processes for preparing the abovementioned N-acyl compounds are known to those skilled in the art. A particularly useful process for preparing polyalkenylsuccinimides is described in the German patent application DE-A-10123553.4, which is fully incorporated
 5 herein by way of reference. In this process, a polyalkenylsuccinic anhydride is reacted first with an alcohol or a phenol and then with an amine. Alternatively, the polyalkenylsuccinic anhydride is reacted with the amine in the presence of an alcohol or a phenol.

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Alcohols suitable for preparing polyalkenylsuccinic imides are preferably monohydric; however, polyhydric alcohols are also suitable.

- 15 Preference is giving to using monohydric alcohols having from 1 to 16 carbon atoms, such as methanol, ethanol, propanol, isopropanol, butanol, sec-butanol, isobutanol, tert-butanol, 2-hydroxymethylfuran, amyl alcohol, isoamyl alcohol, vinylcarbinol, cyclohexanol, n-hexanol, 6-capryl alcohol,
 20 2-ethylhexanol, n-decanol, lauryl alcohol, isooctyl alcohol and their mixtures. Preferred alcohols are those having from 6 to 16 carbon atoms. Particular preference is given to 2-ethylhexanol.

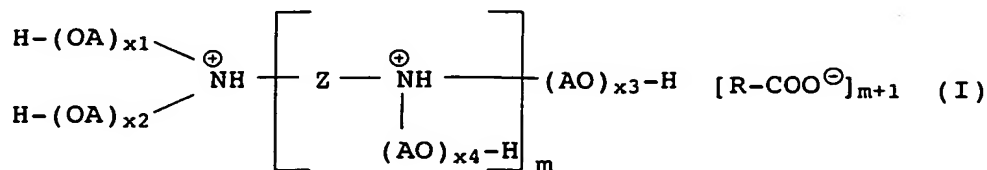
Useful phenols include phenol, naphthol, (o,p)-alkylphenols and
 25 salicylic acid.

Processes for preparing polyalkenyl-substituted carboxylic acids and their derivatives are well known. For instance, the German patent application DE-A-10123553.4 describes the preparation of a
 30 polyolefin-substituted carboxylic acid or a derivative thereof by the reaction of a polyalkene with a monounsaturated acid or its derivative, in which the polyalkylene adds in an ene reaction to the double bond of the acid component.

35 Component B is preferably a fatty acid partly or completely neutralized by amines.

Component B more preferably comprises at least one fatty acid salt of the formula I

40



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where

5 R is C₇-C₂₃-alkyl or a mono- or polyunsaturated C₇-C₂₃-alkenyl, each of which may optionally be substituted by one or more hydroxyl groups;

A is C₂-C₈-alkylene;

10 Z is C₁-C₈-alkylene, C₃-C₈-cycloalkylene, C₆-C₁₂-arylene or C₇-C₂₀-arylalkylene;

m is a number from 0 to 5; and

15 x¹, x², x³ and x⁴ are each independently a number from 0 to 24, where at least one x is not 0,

and optionally at least one further fatty acid RCOOH, where R is as defined above.

20 Such fatty acid salts are described, for example, in WO 01/38463 which is fully incorporated herein by way of reference.

The relatively long-chain R radical occurring in the carboxylate anion RCOO⁻ or in the fatty acid RCOOH is, for example, a branched
25 or preferably linear C₇- to C₂₃-, preferably C₁₁- to C₂₁-, in particular C₁₅- to C₁₉-alkyl group which may additionally bear hydroxyl groups. Examples of parent carboxylic acids include octanoic acid, 2-ethylhexanoic acid, nonanoic acid, decanoic acid, undecanoic acid, dodecanoic acid (lauric acid), tridecanoic
30 acid, isotridecanoic acid, tetradecanoic acid (myristic acid), hexadecanoic acid (palmitic acid), octadecanoic acid (stearic acid) and eicosanoic acid. The acids mentioned may be of natural or synthetic origin. The carboxylate anions may also be based on mixtures of the acids mentioned.

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However, the relatively long-chain R radical occurring in the carboxylate anion RCOO⁻ or in the fatty acid RCOOH is preferably a mono- or polyunsaturated C₇ to C₂₃ radical, especially a mono- or polyunsaturated C₁₁- to C₂₁-, in particular C₁₅- to C₁₉-alkenyl
40 group which may additionally bear hydroxyl groups. These unsaturated radicals are preferably linear. In the case of polyunsaturated alkenyl groups, these preferably contain two or three double bonds. Examples of parent carboxylic acids include elaidic acid, ricinoleic acid, linoleic acid and linolenic acid.
45 Particularly good results are achieved using oleic acid. The carboxylate anions may also be based on mixtures of such unsaturated carboxylic acids with each other and also with the

abovementioned saturated carboxylic acids. Examples of such mixtures include tall oil, tall oil fatty acid and rapeseed oil fatty acid. The unsaturated carboxylic acids mentioned and the mixtures mentioned are generally of natural origin.

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The alkylene group A in compounds of the formula I is preferably derived from appropriate alkylene oxides such as ethylene oxide, 1,2-propylene oxide, 1,2-butylene oxide and cis- or trans-2,3-butylene oxide. However, it may also be 1,3-propylene, 10 1,4-butylene, 1,6-hexylene or 1,8-octylene. A may likewise be a mixture of different groups mentioned. A is more preferably ethylene, 1,2-propylene or 1,2-butylene groups.

The variable Z is in particular C₁- to C₄-alkylene groups such as 15 methylene, 1,2-propylene, 1,2-butylene, 1,3-butylene or 2,3-butylene, C₅- to C₆-cycloalkylene groups such as 1,3-cyclopentylidene or 1,3- or 1,4-cyclohexylidene or C₆- to C₈-arylene or -arylalkylene groups such as 1,3- or 1,4-phenylene, 2-methyl-1,4-phenylene or 1,3- or 1,4-bismethylenephenylene.

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However, the variable Z is preferably a polymethylene group of the formula $-(CH_2)_n-$ where $n = 2$ to 8 , in particular where $n = 2$ to 6 , i.e. in particular 1,2-ethylene, 1,3-propylene, 1,4-butylene, 1,5-pentylene and 1,6-hexylene, but in addition 25 also 1,7-heptylene and 1,8-octylene.

When the variable m is 0, the fatty acid salts used as cationic components in accordance with the invention are generally based, depending on the sum (Σ) of all variables x^1 , x^2 and x^3 , on 30 mixtures of mono-, di- and/or trialkanolamines or pure trialkanolamines. Examples of such alkanolamines include monoethanolamine, diethanolamine, triethanolamine, monoisopropanolamine, diisopropanolamine, triisopropanolamine and also the corresponding mixtures. Within this group, the oleic 35 acid salt of triethanolamine [$(x^1+x^2+x^3) = 3$; A = ethylene] is of particular interest.

However, the variable m is preferably the number 1 or 2. When $m = 1$, the parent molecules are completely and/or partially 40 alkoxylated alkylenediamines such as 1,2-ethylenediamine, 1,3-propylenediamine or 1,4-butylenediamine. When $m = 2$, the parent molecules are usually completely and/or partially alkoxylated dialkylenetriamines such as di(1,2-ethylene)triamine, di(1,3-propylene)triamine or di(1,4-butylene)triamine. Within 45 this group, the bis-oleic acid salts of N,N,N',N'-tetrakis-(2'-hydroxyethyl)-1,2-ethylenediamine ($\Sigma x = 4$) and N,N,N',N'-tetrakis-(2'-hydroxypropyl)-1,2-ethylenediamine (Σx

= 4) and also the tris-oleic acid salts of di(1,2-ethylene)triamine reacted with from 4 to 5 mol of ethylene oxide or 1,2-propylene oxide are of particular interest.

5 However, it is also possible for the amine component on which the fatty acid salts used in accordance with the invention are based to be higher homologs of the alkylenediamine and dialkylenetriamines mentioned, for example triethylenetetramine ($m = 3$), tetraethylenepentamine ($m = 4$) or pentaethylenhexamine
10 ($m = 5$).

In a preferred embodiment, the number x , i.e. the sum of x^1 , x^2 , x^3 and x^4 (Σx), of alkylene oxide units (OA) introduced per amine molecule depends on the number of N-H bonds in the parent amine
15 and may correspond to the number of N-H bonds ($\Sigma x = m+3$). However, it is also possible for more or fewer OA units to be incorporated. In the case of greater than stoichiometric incorporation, a preferred upper limit is a triple alkoxylation per N-H bond [300% of ($m+3$)] with regard to the properties of the
20 resulting fatty acid salts. In the case of less than stoichiometric incorporation, a corresponding preferred lower limit is on average 50% of the alkoxylation [50% of ($m+3$)] ; this results in mixes of species having different degrees of alkoxylation.

25 In a particularly preferred embodiment, the sum (Σ) of all x variables has a value of from 75% to 125% of ($m+3$).

The fatty acid salts of the general formula I can typically be
30 prepared easily by alkoxyating the parent amine by customary methods and subsequently neutralizing with the fatty acids of the formula RCOOH.

When C_2 - to C_4 -alkylene oxides are used, the alkoxylation for the
35 introduction of the first alkylene oxide unit into the N-H bond is advantageously carried out in the presence of small amounts of water (usually from 0.5 to 5% by weight, based on the amount of amine used) without a catalyst at temperatures of from 80 to 140°C, and, for the introduction of further alkylene oxide units,
40 with the exclusion of water in the presence of basic catalysts such as alkali metal hydroxides, e.g. sodium hydroxide or potassium hydroxide, at temperatures of from 100 to 150°C.

The alkoxyated amine obtained in this way is generally
45 neutralized by heating with the appropriate stoichiometric amount or a small stoichiometric deficiency (i.e. from 90 to 100%, in particular from 95 to 100%, of theory) of fatty acid to

temperatures of from 30 to 100°C, in particular from 40 to 80°C, for a period of from 15 minutes to 10 hours, in particular from 30 minutes to 5 hours. The neutralization reaction should be conducted in such a way that no carboxylic ester fractions form in the product. In many cases, both the alkoxyated amine and the fatty acid may be used as liquids which makes the reaction to give the corresponding fatty acid salts particularly simple. The sequence of addition of alkoxyated amine and fatty acid is uncritical, i.e. it is possible to either initially charge the alkoxyated amine and add the fatty acid or initially charge the fatty acid and add the alkoxyated amine.

However, it is also possible in principle to add the alkoxyated amine and the fatty acid as individual components to the additive concentrates or mineral oil products and allow the salt formation to take place there.

The molar ratio of component A to component B in the additive mixture is preferably from 1:10 to 10:1, more preferably from 1:6 to 6:1 and in particular from 1:4 to 4:1.

The present invention further provides the use of the additive mixture described above for additizing fuel and lubricant compositions.

25

Useful fuels are gasoline fuels and middle distillates, such as diesel fuel, heating oil or kerosene, and preference is given to diesel fuel.

30 The diesel fuels are, for example, crude oil raffinates which typically have a boiling range of from 100 to 400°C. These are usually distillates having a 95% point of up to 360°C or even higher. However, these may also be "ultra low sulfur diesel" or "city diesel", characterized by a maximum 95% point of, for example, 345°C and a maximum sulfur content of 0.005% by weight, or by a 95% point of, for example, 285°C and a maximum sulfur content of 0.001% by weight. In addition to the diesel fuels obtained by refining, those obtainable by coal gasification or gas liquefaction ("gas to liquid" (GTL) fuels) are also suitable. 35 Mixtures of the aforementioned diesel fuels with renewable fuels, such as biodiesel or bioethanol, are also suitable. 40

Particular preference is given to using the additive mixture according to the invention for additizing diesel fuels having a low sulfur content, i.e. having a sulfur content of less than 0.05% by weight, preferably of less than 0.02% by weight, in 45

particular of less than 0.005% by weight and especially of less than 0.001% by weight, of sulfur.

Particular preference is given to using the additive mixture
5 according to the invention for reducing carbon deposits caused by burning in the region of the injection system of diesel engines with and without direct fuel injection, preferably of diesel engines having direct fuel injection.

10 Preference is also given to using the additive mixture according to the invention for reducing the corrosive action of a fuel.

The present invention further provides a fuel composition comprising a majority of a hydrocarbon fuel and an effective
15 amount of the additive mixture according to the invention and optionally at least one further additive. With regard to the preferred fuels, reference is made to the above remarks.

The additive mixture according to the invention is preferably
20 present in the fuel in an amount of from 1 to 1000 ppm by weight, more preferably from 10 to 500 ppm by weight and in particular from 50 to 200 ppm by weight, based on the total amount of additivized fuel.

25 The present invention further provides a lubricant composition comprising an effective amount of an additive mixture according to the invention, a lubricant, and also optionally at least one further additive.

30 The invention further provides an additive concentrate comprising the additive mixture according to the invention, at least one solvent or diluent, and also optionally at least one further additive.

35 Examples of useful diluents include the fractions obtained in crude oil processing, such as kerosene, naphtha or brightstock. Furthermore, aromatic and aliphatic hydrocarbons and alkoxyalkanols are suitable. In the case of middle distillates, in particular in the case of diesel fuels, preferably used
40 diluents are naphtha, kerosene, diesel fuels, aromatic hydrocarbons such as Solvent Naphtha heavy, Solvesso® or Shellsol® and also mixtures of these solvents and diluents.

The additive mixture according to the invention is preferably
45 present in the concentrates in an amount of from 0.1 to 80% by weight, more preferably from 1 to 70% by weight and in particular

from 20 to 60% by weight, based on the total weight of the concentrate.

Useful additives which may be present in the fuel or concentrate
5 according to the invention in addition to the additive mixtures according to the invention, in particular for diesel fuels, include detergents, corrosion inhibitors, dehazers, demulsifiers, antifoams, antioxidants, metal deactivators, multifunctional stabilizers, cetane number improvers, combustion improvers, dyes,
10 markers, solubilizers, antistats, other customary lubricity improvers, additives which improve the cold properties, such as flow improvers ("MDFI"), paraffin dispersants ("WASA") and the combination of the two last-mentioned additives ("WAFI").

15 Examples of the customary lubricity improvers include carboxylic acids, especially fatty acids, their esters, especially with polyols, mixtures of these acids and esters, N-acyl compounds which burn ashlessly, such as polyalkenylsuccinamides, mixtures of the abovementioned acids and/or esters with these N-acyl
20 compounds, as described, for example, in WO 96/23855, bis(hydroxyalkyl)fatty amines or hydroxyacetamides.

Examples of useful flow improvers include oil-soluble, polar nitrogen compounds such as ammonium salts and/or amides of mono-
25 or polycarboxylic acids or sulfonic acids and their mixtures with copolymers of ethylene and unsaturated carboxylic esters and optionally comb polymers, as described in WO 95/33805.

The synergistically effective combination of components A and B
30 in the additive mixture according to the invention leads to a distinct improvement in the lubricity of fuels additivized by it and to a distinct reduction in the corrosivity of fuels and carbonization of jets in comparison to prior art additives.

35 The examples which follow illustrate the invention.

Examples

The experiments described hereinbelow were carried out using the
40 following fuels:

- diesel fuel according to DIN EN 590 having a sulfur content of 48 ppm: *diesel I*
- diesel fuel according to DIN EN 590 having a sulfur content
45 of 15 ppm (ULSD): *diesel II*
- diesel fuel according to DIN EN 590 having a sulfur content of 4 ppm (MK1): *diesel III*

- blend of 5% of biodiesel in 95% of diesel I: *blend I*
- blend of 8% of ethanol in 91% of diesel I (1% of stabilizer package): *blend II*
- gas to liquid fuel: *GTL*
- 5 - blend of 20% of GTL in 80% of diesel I: *blend III*

1. Synthesis of the components of the additive mixture

1.1 Synthesis of a polyisobutenesuccinimide (*detergent I*)

10

In a 1 l three-neck flask, 630 g of polyisobutenylsuccinic anhydride (molecular weight of polyisobutene: 1000) (hydrolysis number 95) were mixed with from 0.2 to 2 mol of 2-ethylhexanol and heated to 80 to 160°C within 20 minutes. 105 g (0.55 mol) of
15 tetraethylenepentamine were added. The mixture was stirred at from 150 to 180°C for from 90 to 180 minutes. The alcohol was then removed under reduced pressure.

1.2 Synthesis of a lubricity improver (*lubricity I*)

20

58.4 g (0.2 mol) of
N,N,N',N'-tetrakis-(2'-hydroxypropyl)-1,2-ethylenediamine (obtained from 1,2-ethylenediamine and 4 mol of propylene oxide in the presence of 3% by weight of water, based on the amount of
25 amine used) were heated to 60-80°C and admixed with 110.4 g (0.4 mol) of oleic acid with stirring within two hours. The pH did not fall below 7. Stirring was continued for a further two hours. The product obtained had an N-titer of 2.39 mmol/g.

30

2. Engine experiments

In addition to the combinations according to the invention of *detergent I* and *lubricity I*, detergents customary on the market
35 which are based on polyisobutenesuccinimide and referred to as *detergent II* and lubricity improvers customary on the market which are based on acid and referred to as *lubricity II* or based on ester and referred to as *lubricity III* were used, and their performance was compared with the combinations according to the
40 invention of *detergent I* and *lubricity I*.

2.1 Carbonization of jets in Peugeot XUD 9 according to CEC-F23-A01

45 The flow restriction at a 0.1 mm needle stroke of the abovementioned unadditized base fuels and fuel blends was determined in a Peugeot XUD 9 test engine using the current 10 h

test procedure according to CEC-F23-A01 and compared with the carbonization of the jets observed when the additized fuels and fuel blends were used.

The additized fuels and blends were obtained by adding the
5 abovementioned combinations of 80 mg/kg of detergent I-II and 120 mg/kg of the lubricity improvers lubricity I-III in each case.

The following results were obtained:

10

	Fuel	Detergent	Lubricity improver	Flow restriction at a 0.1 mm needle stroke [%]	Changes **
15	<i>Diesel I</i>	0	0	91.6	
	<i>Diesel II</i>	0	0	91.3	
	<i>Diesel III</i>	0	0	90.5	
	<i>Blend I</i>	0	0	91.6	
20	<i>Blend II</i>	0	0	90.0	
	<i>GTL</i>	0	0	89.9	
	<i>Blend III</i>	0	0	90.3	
	<i>Diesel I</i>	<i>Detergent I</i>	0	64.7	
	<i>Diesel II</i>	<i>Detergent I</i>	0	68.2	
25	<i>Diesel III</i>	<i>Detergent I</i>	0	69.4	
	<i>Blend I</i>	<i>Detergent I</i>	0	74.5	
	<i>Blend II</i>	<i>Detergent I</i>	0	72.3	
	<i>GTL</i>	<i>Detergent I</i>	0	71.4	
30	<i>Blend III</i>	<i>Detergent I</i>	0	68.9	
	<i>Diesel I</i>	<i>Detergent I</i>	<i>Lubricity I</i>	57.6	$\Delta = 7.1$
	<i>Diesel II</i>	<i>Detergent I</i>	<i>Lubricity I</i>	62.7	$\Delta = 5.5$
	<i>Diesel III</i>	<i>Detergent I</i>	<i>Lubricity I</i>	60.6	$\Delta = 8.8$
	<i>Blend I</i>	<i>Detergent I</i>	<i>Lubricity I</i>	68.0	$\Delta = 6.5$
35	<i>Blend II</i>	<i>Detergent I</i>	<i>Lubricity I</i>	64.7	$\Delta = 7.6$
	<i>GTL</i>	<i>Detergent I</i>	<i>Lubricity I</i>	65.1	$\Delta = 6.3$
	<i>Blend III</i>	<i>Detergent I</i>	<i>Lubricity I</i>	62.3	$\Delta = 6.6$
	<i>Diesel I</i>	<i>Detergent II</i>	0	70.8	
	<i>Diesel II</i>	<i>Detergent II</i>	0	73.9	
40	<i>Diesel I</i>	<i>Detergent II</i>	<i>Lubricity II</i>	71.2	$\Delta = -0.4$
	<i>Diesel II</i>	<i>Detergent II</i>	<i>Lubricity II</i>	75.0	$\Delta = -1.1$
	<i>Diesel I</i>	<i>Detergent II</i>	<i>Lubricity III</i>	70.8	$\Delta = 0.0$
	<i>Diesel II</i>	<i>Detergent II</i>	<i>Lubricity III</i>	73.7	$\Delta = 0.2$

45 ** Differences to the flow restriction measured without lubricity improver

Compared to the test results obtained with *detergent I* alone, the combinations according to the invention of *detergent I* and *lubricity I* showed a performance improved by 6-9%. Other combinations resulted in no significant changes being observed.

5

2.2 Corrosion tests according to ASTM D 665 A/B

The corrosion behavior of the abovementioned unadditized base fuels and fuel blends was tested in steel finger tests according to ASTM D 665 A in distilled water and also ASTM D 665 B in synthetic salt water and compared with the corrosion behavior observed when the additized fuels and fuel blends were used.

The additized fuels and blends were obtained by adding the abovementioned combinations of 80 mg/kg of *detergent I-II* and 120 mg/kg of the lubricity improvers *Lubricity I-III* in each case.

The test results were evaluated according to NACE TM-01-72 as follows:

20

A	≈ 100% rust-free
B++	≈ 0.1% or less of the entire surface rusted
B+	≈ 0.1 - 5% of the entire surface rusted
B	≈ 5 - 25% of the entire surface rusted
25 C	≈ 25 - 50% of the entire surface rusted
D	≈ 50 - 75% of the entire surface rusted
E	≈ 75 - 100% of the entire surface rusted

The following results were obtained:

30

	Fuel	Detergent	Lubricity improver	Test according to ASTM D	Corrosion behavior according to NACE TM-01-72**
35	<i>Diesel I</i>	0	0	665 A	C
	<i>Diesel II</i>	0	0	665 A	B
	<i>Diesel III</i>	0	0	665 A	B+
40	<i>Blend I</i>	0	0	665 A	C
	<i>Blend II</i>	0	0	665 A	D
	<i>GTL</i>	0	0	665 A	C
	<i>Blend III</i>	0	0	665 A	C
45	<i>Diesel I</i>	<i>Detergent I</i>	0	665 A	B+
	<i>Diesel II</i>	<i>Detergent I</i>	0	665 A	B++
	<i>Diesel III</i>	<i>Detergent I</i>	0	665 A	A
	<i>Blend I</i>	<i>Detergent I</i>	0	665 A	B+

	Fuel	Detergent	Lubricity improver	Test according to ASTM D	Corrosion behavior according to NACE TM-01-72**
5	<i>Blend II</i>	<i>Detergent I</i>	0	665 A	B
	<i>GTL</i>	<i>Detergent I</i>	0	665 A	B+
	<i>Blend III</i>	<i>Detergent I</i>	0	665 A	B+
	<i>Diesel I</i>	<i>Detergent I</i>	<i>Lubricity I</i>	665 A	A
10	<i>Diesel II</i>	<i>Detergent I</i>	<i>Lubricity I</i>	665 A	A
	<i>Diesel III</i>	<i>Detergent I</i>	<i>Lubricity I</i>	665 A	A
	<i>Blend I</i>	<i>Detergent I</i>	<i>Lubricity I</i>	665 A	A
	<i>Blend II</i>	<i>Detergent I</i>	<i>Lubricity I</i>	665 A	A
	<i>GTL</i>	<i>Detergent I</i>	<i>Lubricity I</i>	665 A	A
15	<i>Blend III</i>	<i>Detergent I</i>	<i>Lubricity I</i>	665 A	A
	<i>Diesel I</i>	<i>Detergent II</i>	0	665 A	C
	<i>Diesel II</i>	<i>Detergent II</i>	0	665 A	B+
	<i>Diesel I</i>	<i>Detergent II</i>	<i>Lubricity II</i>	665 A	B
	<i>Diesel II</i>	<i>Detergent II</i>	<i>Lubricity II</i>	665 A	B+
20	<i>Diesel I</i>	<i>Detergent II</i>	<i>Lubricity III</i>	665 A	B++
	<i>Diesel II</i>	<i>Detergent II</i>	<i>Lubricity III</i>	665 A	B+
	<i>Diesel I</i>	0	0	665 B	E
	<i>Diesel II</i>	0	0	665 B	E
	<i>Diesel I</i>	<i>Detergent I</i>	0	665 B	C
25	<i>Diesel II</i>	<i>Detergent I</i>	0	665 B	B
	<i>Diesel I</i>	<i>Detergent I</i>	<i>Lubricity I</i>	665 B	B++
	<i>Diesel II</i>	<i>Detergent I</i>	<i>Lubricity I</i>	665 B	A

30 Compared to the test results obtained with *detergent I* alone, the combinations according to the invention of *detergent I* and *lubricity I* again showed a distinctly improved performance. Smaller improvements were observed with the other combinations tested.

35

2.3 Determination of lubricity according to HFRR

The lubricity of the unadditized base fuels and fuel blends was tested in HFRR tests according to ASTM D 6079-99, and compared
40 with the lubricity observed when the additized fuels and fuel blends were used.

The additized fuels and blends were obtained by adding the abovementioned combinations of 80 mg/kg of *detergent I* and 120 mg/kg of lubricity improver *lubricity I* in each case. The
45 WS1.4 [μm] which represents the size of the wear patch determined in each case is shown in the table which follows.

The following results were obtained:

	Fuel	Detergent	Lubricity improver	WS1.4 [μm]	Relative improvement [μm] **
5	<i>Diesel I</i>	0	0	633	
	<i>Diesel II</i>	0	0	590	
	<i>Diesel III</i>	0	0	611	
10	<i>Blend I</i>	0	0	251	
	<i>Blend II</i>	0	0	669	
	<i>GTL</i>	0	0	650	
	<i>Blend III</i>	0	0	663	
15	<i>Diesel I</i>	0	<i>Lubricity I</i>	389	
	<i>Diesel II</i>	0	<i>Lubricity I</i>	440	
	<i>Diesel III</i>	0	<i>Lubricity I</i>	470	
	<i>Blend I</i>	0	<i>Lubricity I</i>	268	
	<i>Blend II</i>	0	<i>Lubricity I</i>	520	
20	<i>GTL</i>	0	<i>Lubricity I</i>	420	
	<i>Blend III</i>	0	<i>Lubricity I</i>	403	
	<i>Diesel I</i>	<i>Detergent I</i>	<i>Lubricity I</i>	368	Δ = 21
	<i>Diesel II</i>	<i>Detergent I</i>	<i>Lubricity I</i>	427	Δ = 13
	<i>Diesel III</i>	<i>Detergent I</i>	<i>Lubricity I</i>	445	Δ = 25
25	<i>Blend I</i>	<i>Detergent I</i>	<i>Lubricity I</i>	252	Δ = 16
	<i>Blend II</i>	<i>Detergent I</i>	<i>Lubricity I</i>	499	Δ = 21
	<i>GTL</i>	<i>Detergent I</i>	<i>Lubricity I</i>	415	Δ = 5
	<i>Blend III</i>	<i>Detergent I</i>	<i>Lubricity I</i>	387	Δ = 16

30 ** Differences to WS1.4 values in [μm] measured without detergent

Compared to the test results obtained using *lubricity I* alone, the combinations according to the invention of *detergent I* and *lubricity I* showed a performance improved by 5-25 μm.

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